

SUBCONTRACT TITLE: Innovative Characterization of Amorphous and Thin-Film Silicon for Improved Module Performance

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This report covers the first quarter of Phase II for the period 28 April 2006 to 27 July 2006 of the Thin Film Partnership Subcontract ZXL-5-44205-11. The primary results to be reported from work in my laboratory during this period have come from continuing studies carried out by my post-doc, Shouvik Datta, on a series of four a-Si_{1-x}Ge_x:H samples with roughly 29at.% Ge that were deposited with controlled varying levels of oxygen. These samples were grown by the HWCVD method at NREL and received by us in February 2006.

The NREL a-Si_{1-x}Ge_x:H samples were co-deposited onto both specular stainless steel and p⁺ crystalline Si substrates. Subsequent SIMS analysis indicated oxygen concentrations in the four films deposited with leak rates of (A) 0 (B) 0.02 sccm, (C) 0.06 sccm, and (D) 0.2 sccm were 8×10^{18} , 3×10^{19} , 1×10^{20} , and 5×10^{20} cm⁻³, respectively. Semitransparent Pd Schottky contacts were evaporated onto both types of samples. However, for the films deposited onto c-Si we utilized the buried junction at the substrate for our capacitance based characterization measurements. Figure 1 indicates that, for each pair of co-deposited samples, the spatial uniformity, as revealed by DLCP measurements, is usually much better for the film deposited onto the c-Si substrates than for stainless steel. In addition, as shown in Fig. 2 for the sample with the lowest oxygen level, the Urbach energy was also always smaller for the c-Si substrates samples. We currently believe that the better electronic properties for c-Si substrates compared to stainless steel is due to temperature differences at the growing surface due to the different thermal conductivities of the two types of substrates (for c-Si it is more than 100 times higher than for stainless steel). That is, it is known that the hot filament results in an increasing substrate temperature during growth. The effects of this are clearly evident for the stainless steel substrate (Fig. 1a) which exhibits an increasing defect density as the growth progresses. However, the profile for the c-Si sample (Fig. 1b) is much more uniform which, we believe, reflects a much more constant temperature at the growth surface.

In Fig. 3 we display transient photocapacitance (TPC) spectra presented in our last annual report for 3 of the 4 samples deposited onto the c-Si substrates. As noted previously, there appears to be a systematic decrease in Urbach energy with oxygen at least up to levels of 1×10^{20} cm⁻³ (the 0.06sccm leak rate). In Fig. 4 we display the TPC spectra for the 0 and 0.06 sccm leak rate samples along with transient photocurrent (TPI) spectra taken at the same temperature and rate window. As previously discussed, the TPC spectra correspond to the *difference* of electron and hole carriers collected at each photon energy, while the TPI spectra

FIG. 1. Comparison of drive-level capacitance profiles for HWCVD a-Si_{0.71}Ge_{0.29}:H films co-deposited on crystalline Si and stainless steel substrates. We believe that the much more uniform profile on the c-Si substrate reflects a more constant surface temperature during growth. The slightly larger defect density for the film on the c-Si substrate is probably an artifact due to mis-assigning the device area in this case. That is, the actual effective area is a bit larger than that of the top contact due to area spreading effects through the thickness of the film.

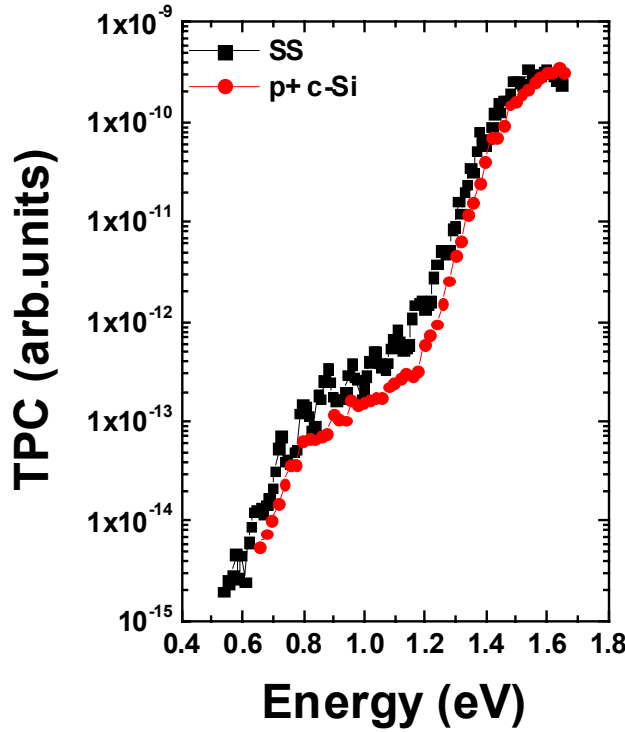
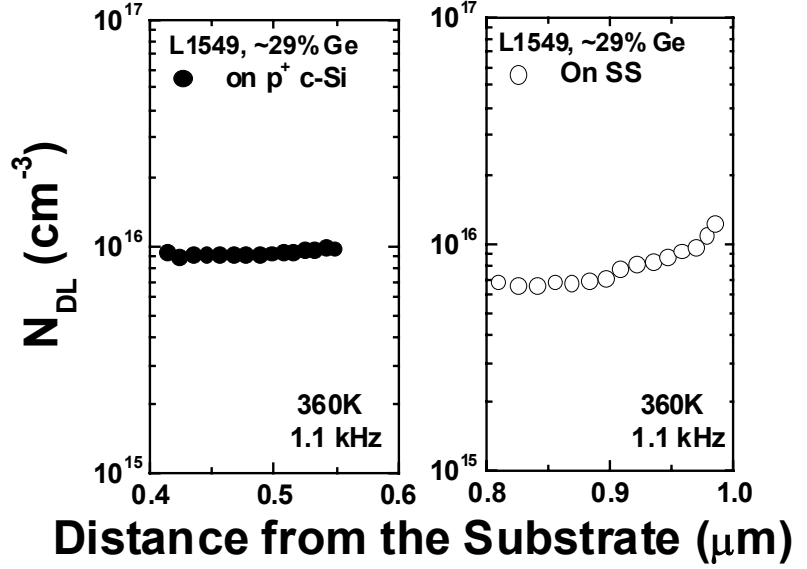


FIG. 2. Comparison of TPC spectra for the 29at.% Ge a-Si_{0.71}Ge_{0.29}:H sample co-deposited on the crystalline Si and Stainless Steel substrates without an intentional air leak. Note the significantly narrower bandtail for film deposited on the c-Si substrate. This indicates a significantly higher degree of structural order possibly due to the higher thermal conductivity of the c-Si substrate.

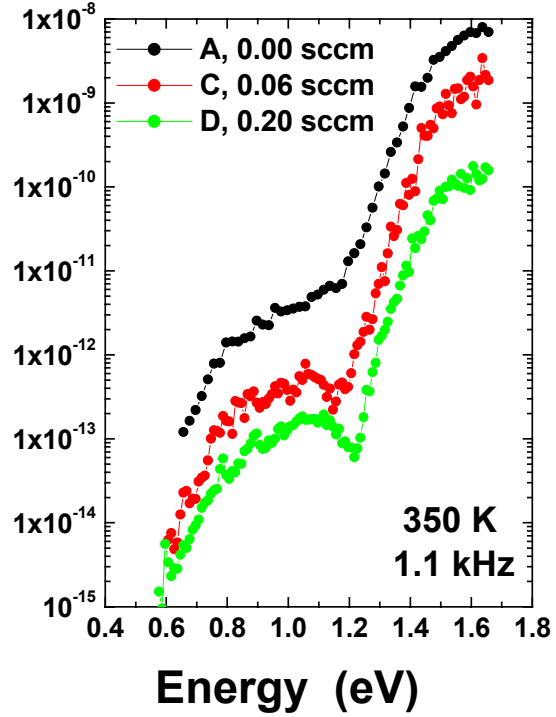


FIG. 3. Comparison of TPC spectra for three a-Si_{0.71}Ge_{0.29}:H samples deposited onto c-Si substrates at varying air leak rates as noted. The best fits of E_U to the exponential region of the bandtails of these 3 samples yield: (A) 42meV, (B) 38meV, and (C) 45meV. However, the values of E_U for samples B and C must be modified on the basis of fits with companion TPI spectra (see Fig. 5).

correspond to the *sum* of these. Thus, by examining both types of spectra together one can deduce the fractions of each. The thin solid lines appearing along with these spectra indicate detailed fits that we have carried out to reproduce their salient features.

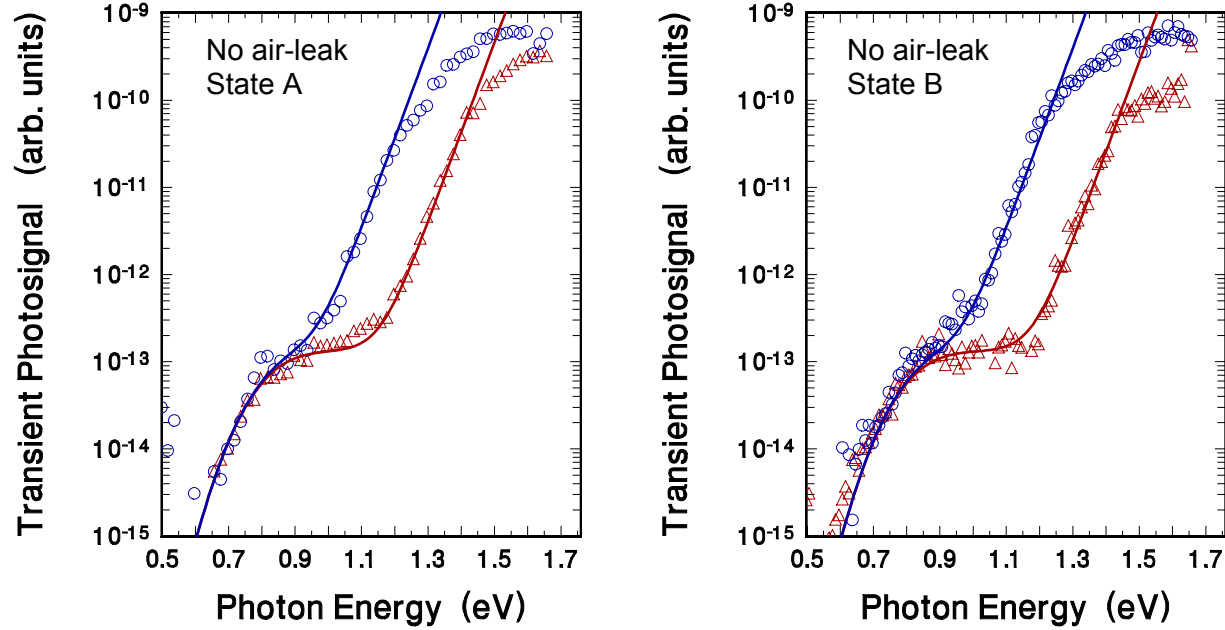


FIG. 4. TPC and TPI spectra before and after light-soaking for the a-Si₃Ge:H deposited without an intentional air leak. The solid lines represent a fit to these spectra indicating a defect band 0.82 eV below E_C with a FWHM of 0.17eV, plus an Urbach energy of 42meV.

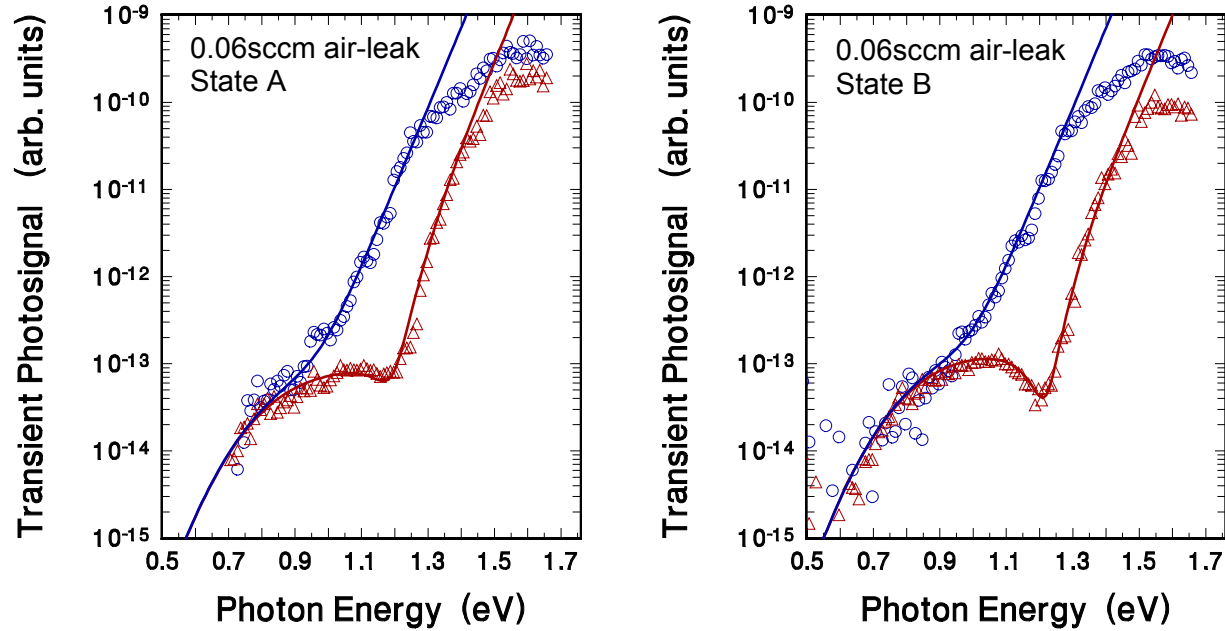


FIG. 5. TPC and TPI spectra before and after light-soaking for the a-Si₃Ge:H deposited with the 0.06 sccm air leak. The fits in this case indicate a defect band 0.85eV below E_C (FWHM = 0.24eV) *plus a second band of defect transitions at 1.43eV above E_V* (also with FWHM = 0.24eV). The deduced Urbach energy that can fit *both* the TPC and TPI spectra is now found to be 47meV.

For the sample deposited without an intentional air leak the spectra indicate two specific features: electronic excitation from a gaussian shaped defect band to the conduction band with an optical energy threshold of 0.82eV (FWHM of 0.17eV), plus a exponential bandtail with an Urbach energy of 42meV. The ratio of the TPI to TPC signals in the bandtail region indicates the relative collection fractions of holes to electrons to holes. It is 99% for this sample, among the highest ever deduced by this method.

The TPC spectra for the sample with the 0.06sccm air leak appears to exhibit an even narrower bandtail (see Fig. 3), and we had previously interpreted it to indicate an Urbach energy of below 40meV. However, when analyzed together with the TPI spectrum in Fig. 5 we have now discovered this is *not* the case. Instead, to obtain a good fit to both types of spectra together we must include the effects of an additional defect band that has an optical threshold centered at 1.43eV *from the valence band*. Taken together with an Urbach energy of 47meV as well as a defect band centered 0.85eV below the conduction band, a very good fit was obtained to both the TPC and TPI spectra as shown. In this case the relative collection fraction of holes/electrons is found to be 95%. This is quite consistent with the 47meV value of Urbach energy that we have deduced in our detailed fitting of these spectra.

A light-soaked state of both samples was examined after exposure to 610nm filtered light from an ELH source for 100hours at an intensity of 1W/cm². The role of the additional defect band is even more apparent in the spectra of the light soaked state of the 0.06sccm air-leak sample that is displayed in Fig. 5. Here we find that it has a similar or perhaps even a slightly smaller magnitude than for State A. The defect band at $E_C - 0.85\text{eV}$, on the other hand, was found to increase, but only by a factor of about 1.5. The same factor increase was found for DLCP data obtained before and after light-soaking of this sample. (The Urbach energy used to obtain the fits to the spectra in the light-soaked state was again 47meV.) Somewhat surprisingly the hole/electron collection fraction appears now to have *increased* (to above 98%).

For the sample without intentional oxygen contamination we also observed an increase in the hole/electron collection fraction (to 99.4%). We found nearly *no change* in the magnitude of the $E_C - 0.82\text{eV}$ defect band. The DLCP data also indicate essentially no change in the midgap defect density after light-soaking.

The above results have been surprising to us in several regards, and we now discuss some of their possible implications. First of all, it is perhaps not surprising to find out from our detailed fits that the Urbach energy is narrowest for the sample with the lowest oxygen impurity level. We suspect that once similar spectra are obtained and analyzed for the 2 remaining samples in this series we will find a systematic trend of increasing Urbach energy with increasing oxygen concentrations. Second, we believe that the additional defect band employed in the fits of Fig. 5 is directly associated with the oxygen impurities in these samples. Indeed, in Fig. 3 it appears that this defect band is even more pronounced in the sample with the 0.2sccm air-leak level. We speculate that this optical transition, 1.43eV from the valence band, is associated with a positively charged oxygen donor level (possibly the previously proposed O_3^+ center, but here we shall simply call it O_D^+) near the conduction band. However, to account for the observed behavior, it is necessary that the electrons that are optically excited into this defect must have the property that they are not quickly thermally emitted into the conduction band. This implies a significant thermal barrier (possibly due to configurational relaxation following the optically

induced electronic occupation) to explain why the subsequent thermal emission of this electron into the conduction band should be inhibited.

Apart from the oxygen impurity related effects, a very notable difference between our results on these HWCVD a-Si_{0.8}Ge_{0.2}:H samples compared to previous such studies on PECVD a-Si_{0.8}Ge_{0.2}:H samples of similar optical gap is that the inferred hole/electron collection ratios do not seemed to be diminished after light-soaking; rather, they actually increase slightly. Moreover, there seems to be very little difference in the midgap defect densities before or after light soaking. This seems to indicate that these HWCVD deposited a-Si_{0.8}Ge_{0.2}:H films are very stable with respect to light-induced degradation. However, there are a couple issues that need to be resolved before such a conclusion can be made definitively.

First, any oxygen related donors (O_D^+) certainly must also lead to an increased D^- defect density; however, as deduced by DLCP, such densities are not large and, moreover, deep hole trapping in the depletion region does not seem to be affected by this. Upon light soaking it may be that some of these O_D^+ are neutralized by changing D^- centers into D^0 's. This might then account for the slight increase in hole collection that we observe. On the other hand, the presence of the O_D^+ centers may also be leading to additional deep electron carrier trapping. In that case the large hole-to-electron collection fractions in these samples might be the result of poorer electron collection instead of improved hole collection. Upon light-soaking, if the O_D^+ was then increased, this would result in a larger hole-to-electron collection fraction simply because the electron collection was diminished further. We are thus planning to carry out more detailed measurements and analysis to see if we can unambiguously distinguish between these two possibilities.

Second, although the D defect density appears to be reasonably low (below $2 \times 10^{16} \text{ cm}^{-3}$ in all cases) and does not appear to increase significantly upon light soaking, it may be that, with the presence of oxygen donors, that many of these D defects are negatively charged. This may then lead to enhanced deep hole trapping and carrier recombination. We consider this unlikely based upon the large hole-to-electron collection fractions that we infer by our TPC/TPI comparisons, but it remains an issue requiring further study. Thus, we are planning some ESR/LESR studies of these films in the near future to try to identify to what degree they may contain significant densities of charged D defects.